

DISSOCIATION OF DIFLUOROETHYLENE CATIONS: AN ION-NEUTRAL COMPLEX ALONG THE FLUOROETHENYLIDENE⁺+HF REACTION PATH

Bernard J. LEYH; Andrée J. LORQUET; Jean-Claude LORQUET; Robert LOCHT

Département de Chimie - Université de Liège - 4000 SART-TILMAN – BELGIUM

The study of the HF loss dissociation channel in singly charged 1,1- and 1,2-difluoroethylene ($C_2H_2F_2^+$) cations by collisional activation (this work) or by photoelectron-photoion coincidence spectroscopy (1) has shown a remarkable behaviour of the kinetic energy released on the $[C_2H,F]^+$ fragment: as the internal energy of the $C_2H_2F_2^+$ parent ion is increased above a given threshold, the average kinetic energy release (KER) decreases. At low internal energy (MI conditions), a dish-topped peak is observed, due to the inverse activation barrier of the $HCCF^+ + HF$ channel, which amounts to about 1 eV. A composite signal, with both a low KER and a high KER component, is observed under CAD conditions. Dissociative photoionization experiments coupled with a retarding potential device have also been performed to get complementary KER data in a wide internal energy range (up to 8 eV).

We suggested that this behaviour could be explained by the opening of a competitive reaction channel leading to the fluoroethenylidene isomer of $[C_2H,F]^+$. We show now that this assumption is successfully checked by high-level *ab initio* calculations.

(i) The fluoroethenylidene cation exists as a minimum on the potential energy surface of the ground $^2A''$ electronic state. It is 1.8 eV more energetic than its conventional fluoroacetylene isomer (QCISD/6-311++G(3df,2pd) level).

(ii) The dissociation path leading to the fluoroethenylidene cation from either 1,2-cis- or 1,2-trans- $C_2H_2F_2^+$ has been studied at different levels, including the B3LYP/AUG-cc-pVTZ and QCISD/6-311++G(3df,2pd) levels. No reverse activation barrier shows up, a result which is compatible with the small KER observed. Furthermore, an ion-neutral complex is evidenced along the reaction path.

References

- (1) F. Güthe, R. Locht, B. Leyh, H. Baumgärtel and K.-M. Weitzel, J. Phys. Chem. A, 103, 8404-8412 (1999)